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Thermochemical properties of complexes of rare earth nitrate with glycine

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Abstract

The combustion energies have been determined for the thirteen solid complexex of rare earth nitrates with glycine. The standard enthalpies of combustion, $\Delta_{c,(coor)}H^{\ominus}$, and standard enthalpies of formation, $\Delta_{f,(coor)}H^{\ominus}$, have been calculated for these complexes. The relationship of $\Delta_{f,(coor)}H^{\ominus}$ with the atomic numbers of the elements in the lanthanide series has been examined. The results show that a certain amount of covalency is present in the chemical bond between the rare earth cation and glycine.

Keywords: Glycine; Rare earth nitrate; Solid complexes; Standard enthalpy of formation

1. Introduction

Great interest has been aroused in the study of complexes of rare earth salts with amino acids because rare earth ions possess some special functions in biochemistry and can be used as a probe to label the calcium ion; moreover amino acids are the structure unit of proteins. Gao and coworkers [1–4] have done much work on the thermodynamics of RE $(NO_3)_3$–Am–H_2O systems (Am is amino acid) using the semimicro method of phase equilibrium study. However, complexes of rare earths with amino acids have rarely been investigated by thermochemical methods. Thus, there are few thermochemical data available in the literature concerning this kind of complex. The standard enthalpies of combustion and standard enthalpies of formation of the complexes have not yet been reported.

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In this paper, combustion energies have been determined for thirteen solid complexes, $RE(Gly)_2(NO_3)_3 \cdot 2H_2O$ (RE is La–Nd, Sm–Er, Yb, Y; Gly is Glycine) using a rotating-bomb calorimeter. The standard enthalpies of combustion, $\Delta_{c,(coor)}H^{\ominus}$, and standard enthalpies of formation, $\Delta_{f,(coor)}H^{\ominus}$, have been calculated for these complexes. The relationship of $\Delta_{f,(coor)}H^{\ominus}$ with the atomic numbers of the elements in the lanthanide series has been examined.

2. Experimental

2.1. Preparation and composition of the complexes

Based on phase equilibrium data, thirteen solid complexes were prepared and put into a desiccator containing P_2O_5 until the weight of the crystals became constant. Chemical analysis proved that the composition of the complexes is $RE(Gly)_2(NO_3)_3 \cdot 2H_2O$ (RE is La–Nd, Sm–Er, Yb, Y), and the purity of $RE(Gly)_2$ $(NO_3)_3 \cdot 2H_2O$ is greater than 99.9% (analytical error, $\leq 0.2\%$; reproducibility, very good).

2.2. Apparatus and experimental procedures

The precision rotating-bomb calorimeter (RBC-type 1) and the basic experimental procedures used in this investigation have already been described [5]. The initial temperature was 25.0000 ± 0.0005°C, and the initial oxygen pressure, 2533.125 kPa. The procedures for analyzing the final products of the bomb were the same as in the literature [6]. Analytical data of the final products show that the combustion reaction is complete, without carbon deposits or carbon monoxide formed in the combustion reaction. The final products were shown to be RE_2O_3 or CeO_2 by IR spectroscopy and chemical analysis. The calorimetric system was calibrated by benzoic acid of standard calorific value prior to use.

2.3. Calculation of the energy equivalent of the RBC-type 1 calorimeter

The energy equivalent of the RBC-type 1 calorimeter was calculated according to the equation

$$W = \frac{Qa + Gb + 5.983\,c}{\Delta T} \tag{1}$$

where W is the energy equivalent of the RBC-type 1 calorimeter (in JK^{-1}), Q is the combustion enthalpy of benzoic acid (in $J\,g^{-1}$), a is the mass of determined benzoic acid (in g), G is the combustion enthalpy of Ni–Cr wire for ignition (in $0.9\,J\,cm^{-1}$), b is the length of actual Ni–Cr wire consumed (in cm), 5.983 is the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 ml of $0.1000\,mol\,dm^{-3}$ solution of NaOH (in $J\,ml^{-1}$), c is the volume (in ml) of consumed $0.1000\,mol\,dm^{-3}$ solution of NaOH and ΔT is the correct value of the temperature rise.

2.4. Correction of the heat exchange

The correct value of the heat exchange was calculated by the equation [7]

$$\Delta(\Delta T) = nV_o + \frac{V_n - V_o}{\bar{T}_n - \bar{T}_o}\left(\frac{T_o + T_n}{2} + \sum_{i=1}^{n-1} T_i - n\bar{T}_o\right) \quad (2)$$

where $\Delta(\Delta T)$ denotes the correct value of the heat exchange, n is the number of readings for the main (or reaction) period, V_o and V_n are the rate of temperature change at the initial and final stage, respectively (V is positive when temperature decreases), $\bar{T}_o$, $\bar{T}_n$ the average temperatures of the calorimeter at the initial and final stages, respectively (average temperature for first and last reading), T_o is the last reading of the initial stage, T_n the first reading of the final stage, $\sum_{i=1}^{n-1} T_i$ the sum of all the readings except the last one of the main period; $(V_n - V_o)/(\bar{T}_n - \bar{T}_o)$ must be constant.

3. Results and discussion

3.1. Calibration of the energy equivalent for the calorimeter

The calorimeter RBC-type 1 was calibrated by benzoic acid of purity 99.999 mol%. Benzoic acid has an isothermal heat of combustion at 25°C of $-26476.0 \pm 5.8\,\mathrm{J\,g^{-1}}$. The calibrated experimental results are summarized in Table 1. The uncertainty is 0.16%.

3.2. Combustion energy of the samples

The method of combustion energy determination for the samples is the same as for the calibration of the calorimeter with benzoic acid. The sample weights were deter-

Table 1
Calibrated experimental results for the energy equivalent of the calorimeter using benzoic acid

No.	Mass of benzoic acid a/g	Calibrated ΔT/K	Calibrated heat of acid containing nitrogen/q_N/J	Calibrated heat of combustion wire q_c/J	Energy equivalent of calorimeter $-W$/kJ K^{-1}
1	1.02220	1.5010	17.38	8.55	18.0459
2	1.14830	1.7023	16.83	5.31	17.8708
3	1.06805	1.5870	19.82	7.65	17.8208
4	1.10430	1.6226	33.67	10.80	18.0227
5	0.90470	1.3278	21.72	9.50	18.0513
6	1.04065	1.5352	20.09	7.70	17.9507
7	0.93050	1.3791	25.52	8.10	17.8931
8	0.98310	1.4571	19.82	5.00	17.8665
9	1.08140	1.5978	22.53	9.45	17.9213

$\bar{W} = -17.9359 \pm 0.0288\,\mathrm{kJ\,K^{-1}}$.

mined in vacuo. The combustion energies of the samples were calculated by the formula

$$\Delta_{c,(coor)}E = \frac{W\Delta T - Gb - 5.983C}{m} \tag{3}$$

where $\Delta_{c,(coor)}E$ denotes the constant-volume combustion energy of the sample, and m is the mass (in g) of the determined sample. The other symbols are as in Eq. (1). The results of the calculations are given in Table 2.

3.3. Standard combustion enthalpies of the complexes

The standard combustion enthalpy of the complexes, $\Delta_{c,(coor)}H^{\ominus}(s)$, refers to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 101.325 kPa

$$\mathrm{RE(Gly)_2(NO_3)_3 \cdot 2H_2O(s)} + \frac{3}{4}\mathrm{O_2(g)} \rightarrow \frac{1}{2}\mathrm{RE_2O_3(s)} + \frac{5}{2}\mathrm{N_2(g)} + \mathrm{CO_2(g)} + 7\mathrm{H_2O(l)}$$

$$(\mathrm{RE\ is\ La, Pr, Nd, Sm\text{–}Er, Yb, Y}) \tag{4}$$

$$\mathrm{Ce(Gly)_2(NO_3)_3 \cdot 2H_2O(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{CeO_2(s)} + \frac{5}{2}\mathrm{N_2(g)} + 4\mathrm{CO_2(g)} + 7\mathrm{H_2O(l)} \tag{5}$$

Table 2
Combustion energy, standard combustion enthalpy and standard enthalpy of formation of complexes $\mathrm{RE(Gly)_2(NO_3)_3 \cdot 2H_2O}$

Complex	Number of experiments	$-\Delta_{c,coor(s)}E$/J g^{-1}	$-\Delta_{c,coor(s)}H^{\ominus}$/kJ mol^{-1}	$-\Delta_{c,coor(s)}H^{\ominus}$/kJ mol^{-1}
$\mathrm{La(Gly)_2(NO_3)_3 \cdot 2H_2O}$	6	3577.02 ± 5.54	1813.97 ± 2.83	2657.28 ± 6.11
$\mathrm{Ce(Gly)_2(NO_3)_3 \cdot 2H_2O}$	6	3749.62 ± 5.37	1907.32 ± 2.75	2755.91 ± 7.02
$\mathrm{Pr(Gly)_2(NO_3)_3 \cdot 2H_2O}$	6	3686.42 ± 5.33	1877.65 ± 2.84	2610.79 ± 5.89
$\mathrm{Nd(Gly)_2(NO_3)_3 \cdot 2H_2O}$	6	3826.83 ± 5.89	1962.02 ± 3.04	2516.68 ± 5.79
$\mathrm{Pm(Gly)_2(NO_3)_3 \cdot 2H_2O}$	–	–	–	2376*
$\mathrm{Sm(Gly)_2(NO_3)_3 \cdot 2H_2O}$	5	4371.38 ± 6.51	2269.99 ± 3.40	2212.35 ± 5.18
$\mathrm{Eu(Gly)_2(NO_3)_3 \cdot 2H_2O}$	5	3627.70 ± 5.74	1887.19 ± 2.85	2518.95 ± 5.67
$\mathrm{Gd(Gly)_2(NO_3)_3 \cdot 2H_2O}$	7	3659.07 ± 5.52	1922.99 ± 2.92	2559.45 ± 6.31
$\mathrm{Tb(Gly)_2(NO_3)_3 \cdot 2H_2O}$	5	3718.36 ± 5.76	1960.90 ± 3.06	2550.04 ± 5.82
$\mathrm{Dy(Gly)_2(NO_3)_3 \cdot 2H_2O}$	6	3768.29 ± 5.61	2000.89 ± 3.00	2506.45 ± 7.67
$\mathrm{Ho(Gly)_2(NO_3)_3 \cdot 2H_2O}$	6	3247.44 ± 4.84	1730.00 ± 2.30	2785.21 ± 7.02
$\mathrm{Er(Gly)_2(NO_3)_3 \cdot 2H_2O}$	6	3491.49 ± 5.27	1869.22 ± 2.84	2654.33 ± 5.68
$\mathrm{Tm(Gly)_2(NO_3)_3 \cdot 2H_2O}$	–	–	–	2403*
$\mathrm{Yb(Gly)_2(NO_3)_3 \cdot 2H_2O}$	6	4539.22 ± 6.76	2460.65 ± 3.68	2021.25 ± 4.71
$\mathrm{Lu(Gly)_2(NO_3)_3 \cdot 2H_2O}$	–	–	–	1438*
$\mathrm{Y(Gly)_2(NO_3)_3 \cdot 2H_2O}$	6	4435.90 ± 7.09	2031.10 ± 3.27	2496.34 ± 5.99

* Estimated value.

The standard combustion enthalpies of the above complexes were calculated from the combustion energy by the equation

$$\Delta_{\mathrm{c,coor(s)}}H^{\ominus} = \Delta_{\mathrm{c,coor(s)}}E + \Delta nRT \tag{6}$$

$$\Delta n = n_{\mathrm{gas}}(\text{products}) - n_{\mathrm{gas}}(\text{reactants})$$

where n_{gas} is the total amount (in moles) of gas present as products or as reactants, $R = 8.314\,\mathrm{J\,mol^{-1}K^{-1}}$, $T = 298.15\,\mathrm{K}$. The results of the calculations are also shown in Table 2.

3.4. *Standard formation enthalpies of the complexes*

The standard formation enthalpies of the above complexes were calculated by Hess's law according to the thermochemical equations

$$\Delta_{\mathrm{f,coor(s)}}H^{\ominus} = \frac{1}{2}\Delta_{\mathrm{f,RE_2O_3(s)}}H^{\ominus} + 4\Delta_{\mathrm{f,CO_2(g)}}H^{\ominus} + 7\Delta_{\mathrm{f,H_2O(l)}}H^{\ominus} - \Delta_{\mathrm{c,coor(s)}}H^{\ominus} \tag{7}$$

(RE is La, Pr, Nd, Sm–Er, Yb, Y)

$$\Delta_{\mathrm{f,coor(s)}}H^{\ominus} = \Delta_{\mathrm{f,CeO_2(s)}}H^{\ominus} + 4\Delta_{\mathrm{f,CO_2(g)}}H^{\ominus} + 7\Delta_{\mathrm{f,H_2O(l)}}H^{\ominus} - \Delta_{\mathrm{c,coor(s)}}H^{\ominus} \tag{8}$$

$\Delta_{\mathrm{f,RE_2O_3(s)}}H^{\ominus} = -1793.14 \pm 0.79$(La), -1827.60(Pr), -1808.12 ± 1.00(Nd), -1815.40 ± 2.01(Sm), -1663.00(Eu), -1815.60 ± 3.60(Gd), -1827.60(Tb), -1865.39 ± 3.89(Dy), -1881.13 ± 5.02(Ho), -1897.82 ± 1.88(Er), -1814.52 ± 2.22(Yb) and $-1905.60 \pm 2.26\,\mathrm{kJ\,mol^{-1}}$(Y) [8]; $\Delta_{\mathrm{f,CO_2(g)}}H^{\ominus} = -393.51 \pm 0.13\,\mathrm{kJ\,mol^{-1}}$ [9]; $\Delta_{\mathrm{f,H_2O(l)}}H^{\ominus} = -285.83 \pm 0.042\,\mathrm{kJ\,mol^{-1}}$[9]; $\Delta_{\mathrm{f,CeO_2(s)}}H^{\ominus} = -1088.59 \pm 1.38\,\mathrm{kJ\,mol^{-1}}$[9].

The results of the calculations are also shown in Table 2. Corresponding data for three other complexes $\mathrm{RE(Gly)_2(NO_3)_3 \cdot 2H_2O}$ (where RE is Pm, Tm, Lu) were estimated by interpolation, and these data are also given in Table 2.

In Fig. 1, $\Delta_{\mathrm{f,coor(s)}}H^{\ominus}$ values of the above complexes are plotted against the atomic numbers of the elements in the lanthanide series. It is seen from Fig. 1 that the curve shows the so-called "tripartite effect". The point corresponding to complex ($\mathrm{Ce(Gly)_2(NO_3)_3 \cdot 2H_2O}$) is a considerable deviation from the curve due to its final product being

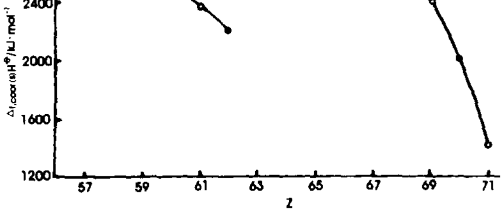

Fig. 1. Plot of $\Delta_{\mathrm{f,coor(s)}}H^{\ominus}$ values against the atomic numbers of the lanthanoids.

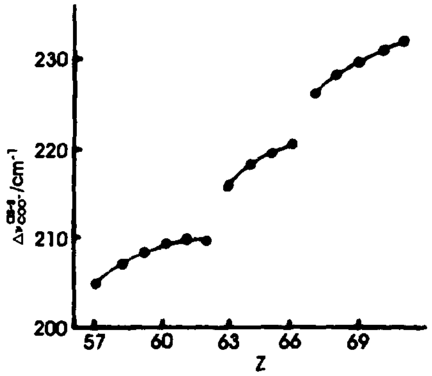

Fig. 2. Plot of $\Delta\nu^{as-s}_{coo^-}$ against the atomic number of the lanthanoids for the complexes ($\Delta\nu^{as-s}_{coo^-}$ is the difference between $\nu^{as}_{coo^-}$ and $\nu^{s}_{coo^-}$ in IR spectra for the complexes).

CeO_2 when $Ce(Gly)_2(NO_3)_3 \cdot 2H_2O$ was combusted. The observed "tripartite effect" is consistent with the observed result in the IR spectra (Fig. 2). The results show that a certain amount of covalence is present for the chemical bond between the rare earth cations and glycine.

References

[1] X.W. Jiang, Y.M. Chen and S.L. Gao, Chinese Sci. Bull. (China), 38(12) (1993) 1006.
[2] X.W. Jiang, Y.M. Chen and S.L. Gao, J. Inorg. Chem. (China), 9(1) (1993) 111.
[3] S.L. Gao, D.H. Ren, C.C. Liu, et al., Chinese Sci. Bull. (China), 38(24) (1993) 2048.
[4] G.C. Dang, X.F. Wang, F.Y. Ding, et al., J, Chinese Rare Earth Soc. (China), 13(1) (1995) 90.
[5] X.F. Yang, X.W. Yang and L.Z. Sun, Chem. J. Chinese Univ. (China), 7(4) (1986) 363.
[6] X.F. Yang, X.W. Yang and L.Z. Sun, Xian Chem. Tech. (China), 3(1986) 6.
[7] M.M. Popov, Thermometry and Calorimetry, Mosco Univ. Publishing House, Mosco, 1954, p. 382.
[8] E.J. Huber and C.E. Hollcy, Experimental Thermochemistry, Vol. II, Interscience Publishers, New York, 1961, p. 77.
[9] J.D. Cox, J. Chem. Thermodyn, 10 (1978) 903.